

This listing of claims will replace all prior versions of claims in this Application.

Listing of Claims

Claim 1. (Currently Amended) An electrolytic copper plating solution suitable for filling vias in a substrate with copper, the solution comprising copper, water, a water-soluble chlorine compound, a brightening agent compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, and

a thiol-reactive compound chosen from performic acid, peracetic acid, peroxypropionic acid, peroxybutanoic acid or peroxypentanoic acid ~~peroxy acids, or carboxylic acids~~, wherein the carboxylic acids are chosen from formic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, citraconic acid or mesaconic acid.

Claim 2. (Previously Amended) The electrolytic copper plating solution according to claim 1, wherein the compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, is selected from the group consisting of:

- (1) M-SO₃-(CH₂)_a-S-(CH₂)_b-SO₃-M;
- (2) M-SO₃-(CH₂)_a-O-CH₂-S-CH₂-O-(CH₂)_b-SO₃-M;
- (3) M-SO₃-(CH₂)_a-S-S-(CH₂)_b-SO₃-M;
- (4) M-SO₃-(CH₂)_a-O-CH₂-S-S-CH₂-O-(CH₂)_b-SO₃-M;
- (5) M-SO₃-(CH₂)_a-S-C(=S)-S-(CH₂)_b-SO₃-M;
- (6) M-SO₃-(CH₂)_a-O-CH₂-S-C(=S)-S-CH₂-O-(CH₂)_b-SO₃-M;

- (7) A-S-(CH₂)_a-SO₃-M; and
- (8) A-S-CH₂-O-(CH₂)_a-SO₃-M

wherein each of a and b represents an integer in the range of 3 to 8; M represents a hydrogen or alkali metal element; and A represents: a hydrogen atom; an alkyl group having 1 to 10 carbon atoms; an aryl group; an acyclic or cyclic amine compound containing 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms; or a heterocyclic compound containing 1 to 2 sulfur atoms, 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms.

Claim 3. (Original) The electrolytic copper plating solution according to claim 1, wherein the electrolytic copper plating solution contains 0.1 to 100 mg/L of the compound having the structure represented by the formula of -X-S-Y-.

Claim 4. (Canceled)

Claim 5. (Previously Presented) The electrolytic copper plating solution according to claim 1, wherein the thiol-reactive compound is present in the electrolytic copper plating solution in an amount from 1.0×10^{-4} to 1.0×10^{-1} mol/L.

Claim 6. (Currently Amended) A process for filling vias in a substrate by electrolytic copper plating comprising contacting the substrate with the an electrolytic copper plating solution of claim 1comprising copper, water, a water-soluble chlorine compound, a brightening agent compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, and
a thiol-reactive compound chosen from peroxy acids, aliphatic aldehyde compounds, alicyclic aldehyde compounds, aliphatic ketone compounds, alicyclic ketone compounds, hydrogen peroxide or carboxylic acids; wherein the carboxylic acids are chosen from formic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, citraconic acid or mesaconic acid, and applying an anodic current density of

0.1 to 10 A/dm² and maintaining a concentration of a compound having -X-S- structure equal or less than 2.0 micro mol/L.

Claim 7. (Previously Presented) The process of claim 6, wherein the substrate is a printed wiring board or a wafer.

Claims 8-9. (Canceled)

Claim 10. (Currently amended) A method for filling vias in a substrate with copper comprising controlling by electrolytic copper plating comprising contacting the substrate with an electrolytic copper plating solution comprising copper, water, a water-soluble chlorine compound, a brightening agent compound having the structure represented by the formula of -X-S-Y-

wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, and

a thiol-reactive compound chosen from peroxy acids, aliphatic aldehyde compounds, alicyclic aldehyde compounds, aliphatic ketone compounds, alicyclic ketone compounds, hydrogen peroxide or carboxylic acids; wherein the carboxylic acids are chosen from formic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, citraconic acid or mesaconic acid,

by adding the thiol reactive compound to the electrolytic copper plating solution and maintaining a concentration of a compound having -X-S- structure equal or less than 1.0 micro mol/L and applying an anodic current density of 0.1 to 10 A/dm².

Claim 11. (Previously Amended) The method according to claim 10, wherein the compound having the structure represented by the formula of -X-S-Y- wherein each of X and Y independently represents an atom selected from the group consisting of a hydrogen atom, a carbon atom, a sulfur atom, and a nitrogen atom, in which X and Y may represent the same only in the case of a carbon atom, is selected from the group consisting of:

- (1) M-SO₃-(CH₂)_a-S-(CH₂)_b-SO₃-M;

- (2) $M-SO_3-(CH_2)_a-O-CH_2-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (3) $M-SO_3-(CH_2)_a-S-S-(CH_2)_b-SO_3-M$;
- (4) $M-SO_3-(CH_2)_a-O-CH_2-S-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (5) $M-SO_3-(CH_2)_a-S-C(=S)-S-(CH_2)_b-SO_3-M$;
- (6) $M-SO_3-(CH_2)_a-O-CH_2-S-C(=S)-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (7) $A-S-(CH_2)_a-SO_3-M$; and
- (8) $A-S-CH_2-O-(CH_2)_a-SO_3-M$

wherein each of a and b represents an integer in the range of 3 to 8; M represents a hydrogen or alkali metal element; A represents: a hydrogen atom; an alkyl group having 1 to 10 carbon atoms; an aryl group; an acyclic or cyclic amine compound containing 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms; or a heterocyclic compound containing 1 to 2 sulfur atoms, 1 to 6 nitrogen atoms, 1 to 20 carbon atoms, and a plurality of hydrogen atoms.

Claims 12-14. (Canceled)

Claim 15. (Previously Presented) The electrolytic copper plating solution according to claim 1, wherein the copper comprises copper sulfate, copper cyanide or copper pyrophosphate.

Claim 16. (Canceled)

Claim 17. (Previously Amended) The process according to claim 6, wherein the peroxy acids are chosen from performic acid, peracetic acid, peroxypropionic acid, peroxybutanoic acid or peroxypentanoic acid.

Claim 18. (Previously Presented) The process according to claim 6, wherein the copper comprises copper sulfate, copper cyanide or copper pyrophosphate.

Claim 19. (Previously Amended) The method according to claim 10, wherein the aliphatic aldehyde compounds are chosen from formaldehyde, glutaraldehyde, acetaldehyde, propionaldehyde, malonaldehyde, succinaldehyde, or glyoxal.

Claim 20. (Previously Presented) The process of claim 6 wherein the vias are filled without voids.